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TITLE: Relaxation Dynamics of Excited States of Er[3+] in YVO4 Single Crystals

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TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

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# Relaxation dynamics of excited states of $\text{Er}^{3+}$ in $\text{YVO}_4$ single crystals

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## ABSTRACT

Crystals of  $\text{Er}:\text{YVO}_4$  were grown by Czochralski method. Uniformly doped and good quality crystals have been obtained. The lifetimes of the  $^4\text{S}_{3/2}$ , and the luminescence dynamics were studied as a function of temperature in the region 5–500K. The green luminescence around 550 nm has been observed in excitation by the Ti:sapphire laser into  $^4\text{I}_{11/2}$  level. The excitation spectrum recorded for  $^4\text{S}_{3/2}$  has been compared with absorption cross section spectrum and calculated ESA spectrum for  $^4\text{I}_{11/2}-^4\text{F}_{7/2}$  transition. The contribution of ESA process in upconversion phenomenon under excitation into  $^4\text{I}_{11/2}$  has been assessed. The emission cross-section and the gain coefficient for  $^4\text{I}_{13/2}-^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  in  $\text{YVO}_4$  have been calculated.

**Keywords:**  $\text{Er}:\text{YVO}_4$  crystals, absorption spectrum, green luminescence, doping.

## 1. INTRODUCTION

In the last few years  $\text{Er}^{3+}$  doped  $\text{YVO}_4$  has been considered as a potential laser material in the IR spectral region<sup>1</sup>. However, that real potential strongly depends on the relaxation dynamics of excited states to lower states and upconversion processes. For  $\text{Er}:\text{YVO}_4$  the ESA and SE cross-section spectra for  $^4\text{I}_{13/2}-^4\text{I}_{15/2}$  the transition do not overlap<sup>2</sup>. Accordingly, losses of radiation by ESA at potential laser transition should be negligible but no laser emission of  $\text{Er}^{3+}:\text{YVO}_4$  has been observed yet. The absorption spectra, emission spectra and fluorescence dynamics of  $\text{Er}^{3+}:\text{YVO}_4$  have been reported<sup>3</sup>. Upconverted green luminescence has been observed by excitation into  $^4\text{F}_{9/2}$ ,  $^4\text{I}_{9/2}$ , and  $^4\text{I}_{11/2}$ <sup>1</sup>. The absorption cross-section ( $\sigma_{\text{ESA}}$ ) from  $^4\text{I}_{13/2}$  level of  $\text{Er}:\text{YVO}_4$  have been determined experimentally<sup>3</sup>. In this study, the temperature dependence of  $^4\text{S}_{3/2}$  decay in the range 5-500K was investigated and compared with predictions of multiphonon relaxation model. The contribution of ESA process to the upconversion phenomenon under excitation into  $^4\text{I}_{11/2}$  was considered. The emission cross-section and the gain coefficient for  $^4\text{I}_{13/2}-^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  in  $\text{YVO}_4$  were calculated.

## 2. EXPERIMENTAL

Crystals of  $\text{Er}:\text{YVO}_4$  were grown by Czochralski method. Uniformly doped and good quality crystals have been obtained. The concentration of  $\text{Er}^{3+}$  in the crystals studied was 0.5, 2, and 4 at %. Absorption spectra were measured with a Varian model 2300 absorption spectrophotometer. The sample luminescence was excited by a Ti:sapphire laser emitting at 970 nm or by Continuum OPO model Surelite I pumped by third harmonic of Nd:YAG laser and dispersed by 1m double grating monochromator, detected by photomultiplier or InSb detector and analysed by a Stanford Model SRS 250 Boxcar integrator. In luminescence decay measurements a digital oscilloscope Tektronix model TDS 3052 has been used. For low temperature measurements, the samples were mounted in Oxford Model CF 1204 continuous flow liquid helium cryostat equipped with a temperature controller.

## 3. RESULTS AND DISCUSSION

Room temperature absorption spectrum of  $\text{Er}^{3+}$  ions on  $\text{YVO}_4$  is shown in Fig.1. The observed absorption lines are not fully resolved and inhomogeneously broadened.

The temperature dependence of luminescence lifetime of the  $^4S_{3/2}$  level of  $Er^{3+}$  in  $YVO_4$  for samples containing 0,5at % and 4 at % of erbium is shown by solid circles and squares respectively in Fig.2. The samples were excited by OPO at 523 nm into the level  $^2H_{11/2}$ . The obtained data are consistent with data presented previously for room temperature and at 77K <sup>3,4</sup>. In the phenomenological approach of Riseberg and Moos <sup>5</sup> the expected temperature dependence of  $^4S_{3/2}$  lifetime has been drawn according to the formula:

$$\tau = \frac{12A_r(^2H_{11/2})\exp\left(-\frac{\Delta E}{kT}\right) + 4A_r(^4S_{3/2})}{12\exp\left(-\frac{\Delta E}{kT}\right) + 4} + A_0 \left( \frac{\exp \frac{\hbar\omega}{kT}}{\exp \frac{\hbar\omega}{kT} - 1} \right)^p \quad (1)$$

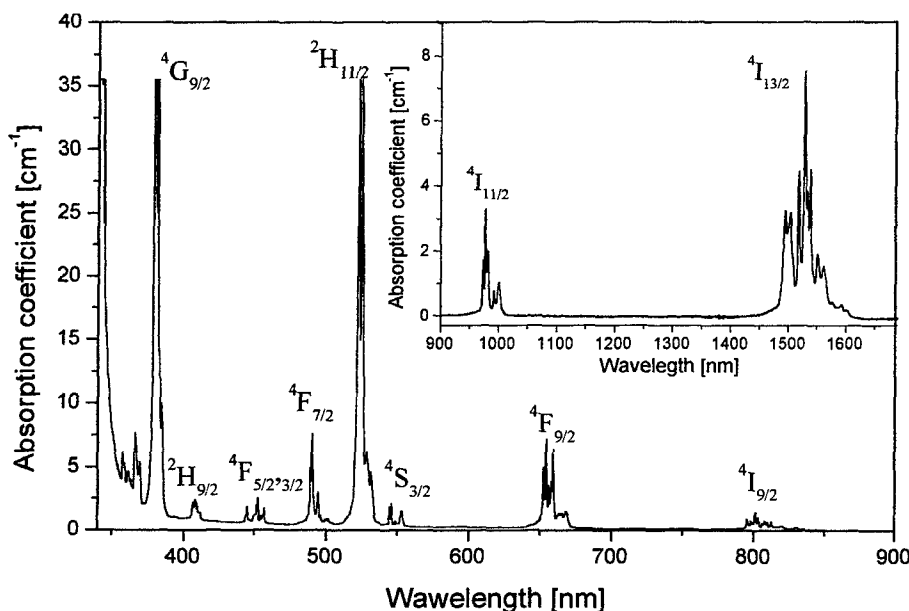


Fig. 1 Absorption spectrum of  $Er^{3+}$  ions in  $YVO_4$  crystal recorded at room temperature.

where:  $A(^2H_{11/2})$ ,  $A_r(^4S_{3/2})$  denote the values of the radiative transition rates as given in <sup>4</sup>,  $\Delta E=709 \text{ cm}^{-1}$  is the energy gap between  $^2H_{11/2}$  and  $^4S_{3/2}$  levels.  $A_0$  denotes the spontaneous multiphonon transition rate,  $\hbar\omega=890 \text{ cm}^{-1}$  is the phonon energy <sup>6</sup> and  $p=4$  is the number of phonons needed to cover the energy gap between  $^4S_{3/2}$  and  $^4F_{9/2}$  levels.  $A_0$  has been calculated from the inverse of luminescence lifetime measured and 5K. The solid line in Fig.2 presents the theoretical approach derived from equation (1). It cannot predict the experimental temperature dependence of lifetime for the  $^4S_{3/2}$  level because the experimentally determined lifetime decreases quickly with increasing temperature. The reason of

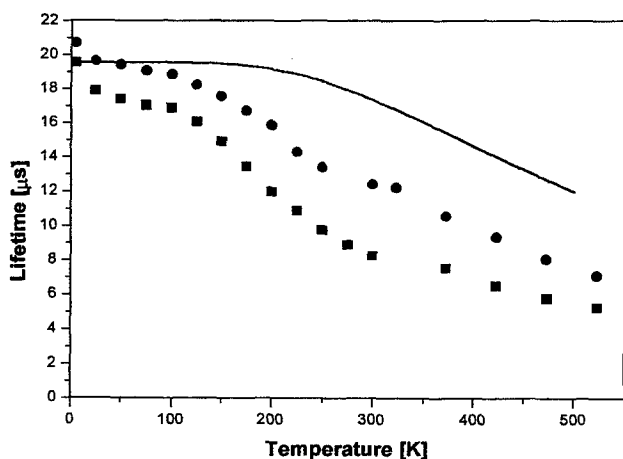


Fig. 2 Temperature dependence of luminescence lifetime of the  $^4S_{3/2}$  level of  $Er^{3+}$  in  $YVO_4$  crystal. Data indicated by solid circles and squares for samples containing 0.5 at % and 4 at % of erbium, respectively. See text for the explanation of theoretical line.

observed discrepancy is not clear yet. This may be caused by interaction of active ions with structural defects.

To elucidate a mechanism of upconversion the excitation spectrum of  $^4S_{3/2}$  luminescence was recorded at room temperature. The sample was excited by tuneable Ti:sapphire laser in the range 968-988 nm and detected at 552.5nm. The resulting excitation spectrum is presented in Fig.3 by solid line with the  $\sigma_{GSA}$  spectrum (dotted line) in the same wavelength domain. From the analysis of the energy level diagram of  $Er^{3+}$  in  $YVO_4$  presented in <sup>3</sup>, we have built the  $\sigma_{ESA}$  spectra corresponding to  $^4I_{11/2} \rightarrow ^4F_{7/2}$  transition after pumping around 970 nm using the expression <sup>7</sup>.

$$\sigma_{ESA}^{J \rightarrow J'}(\lambda) = \lambda S_{calc} (J - J') \sum_{i,j} \frac{f_i}{2J+1} \frac{1}{\pi} \frac{\Delta\lambda/2}{(\lambda - \lambda_{ij})^2 + (\Delta\lambda/2)^2} \quad (2)$$

where :  $f_i$  is the Boltzmann factor for  $i$ -th crystal field level of the starting multiplet  $J$  of ESA transition. This factor has been approximated by  $1/(2J+1)$ ;  $\lambda_{ij}$  are the expected wavelength position of ESA lines. In order to calculate  $\lambda_{ij}$ , the experimentally observed crystal-field energy levels of  $Er^{3+}$  ion in  $YVO_4$ , for the  $^4I_{11/2}$  and  $^4F_{7/2}$  were taken from Table 3 in<sup>3</sup>.  $\Delta\lambda$  is the linewidth of ESA line assumed to has a Lorentzian profile and the same as of GSA line around 970 nm i.e.  $\Delta\lambda=1nm$ ;  $\lambda$  is the average wavelength of the transition  $\lambda=9.74 \times 10^{-5}cm$ .  $S_{calc}$  has been calculated by using expression:

$$S_{calc} = C(n) S(^4I_{11/2} - J') \quad (3)$$

$$\text{where: } C(n) = \frac{(n^2 + 2)^2}{9n} \frac{2\pi^3 e^2}{3hc} \quad (4)$$

$$\text{and } S(^4I_{11/2} - J') = \sum_{i=2,4,6} \Omega_i \left| \langle ^4I_{11/2} \| U^{(i)} \| J' \rangle \right|^2 \quad (5)$$

$S$  is the electric - dipole transition strength,  $U^{(i)}$  are matrix elements and  $\Omega_i$  are Judd-Ofeld parameters.  $S_{calc}$  was calculated taking to account  $\Omega_i$  parameters from<sup>3</sup>,  $S_{calc}=0.893$  and  $C(n)=0,0283$  for  $YVO_4$  ( $n=2.02$ ). In this calculation it is assumed that all transitions between the Stark components have the same intensity and the same polarisation.

The resulting spectrum is presented in Fig.3 by bold line. It can be seen that the excitation spectrum coincides with both the ESA transition and GSA transition lines. The overlap with the  $\sigma_{GSA}$  is weaker than with  $\sigma_{ESA}$ . Thus, we conclude that the losses by ESA from  $^4I_{11/2}$  when exciting at 970nm may be appreciable. It was reported<sup>8</sup> that in  $Er^{3+}$  doped fluorozirconate glasses, ESA processes were the principal processes for the upconversion emission near 550nm.

To determine the emission cross section for  $^4I_{13/2} - ^4I_{15/2}$  transition of  $Er^{3+}$  in  $YVO_4$  we have used the reciprocity method<sup>9</sup>. This method is based on the relation between absorption cross section  $\sigma_a(\lambda)$  and emission cross section  $\sigma_{em}(\lambda)$  by the following relation

$$\sigma_{em}(\lambda) = \frac{Z_{low}}{Z_{up}} \sigma_a(\lambda) \exp\left(\frac{Z_{ZL} - E(\lambda)}{k_B T}\right) \quad (6)$$

where:  $Z_{low}$ ,  $Z_{up}$  are the partition functions of lower and upper level, respectively, defined as

$$Z_{low} = \sum_{i=1}^n g_i \exp\left(\frac{-E_i}{k_B T}\right) \quad Z_{up} = \sum_{j=1}^n g_j \exp\left(\frac{-(E_j - E(\lambda))}{k_B T}\right)$$

where:  $g_i(g_j)$  is a degeneration of sublevel,  $E_i(E_j)$  is the energy of the sublevel,  $E_{ZL}$  is an energy separation between the lowest crystal field components of the upper and lower multiplets, and  $k_B$  is the Boltzmann constant. The ratio  $Z_{low}/Z_{up}$  calculated using the above values is equal to 1.06. The energies of  $E_i$  and  $E_j$  Stark sublevels for  $^4I_{15/2}$  and  $^4I_{13/2}$  were taken from Table 3 in<sup>3</sup>. Calculated

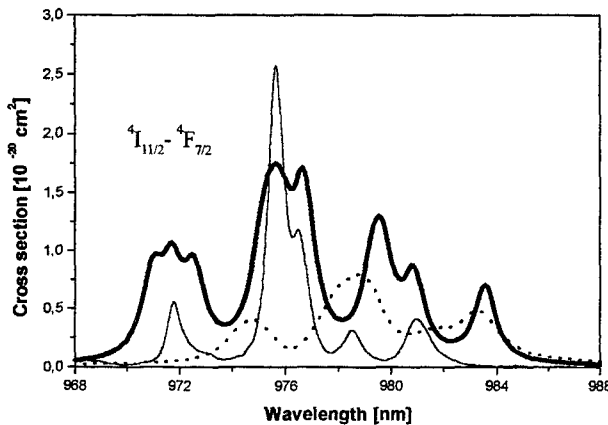


Fig. 3 Room temperature excitation spectrum of  $^4S_{3/2}$  luminescence of  $Er^{3+}$  in  $YVO_4$  - solid line with  $\sigma_{GSA}$  spectrum for  $^4I_{15/2} - ^4I_{13/2}$  (dotted line). For the comparison, the calculated spectrum for  $\sigma_{ESA}$   $^4I_{11/2} - ^4F_{7/2}$  transition is presented - bold line.

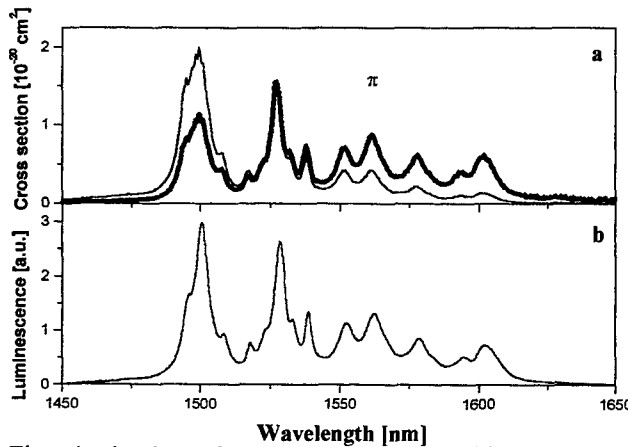


Fig. 4 a) absorption cross section (solid line) and calculated spectra and emission cross section (bold line) b) luminescence spectra recorded for  $^4I_{13/2} - ^4I_{15/2}$  under excitation by Ti:sapphire laser emitting at 970 nm. All spectra for  $\pi$  polarisation

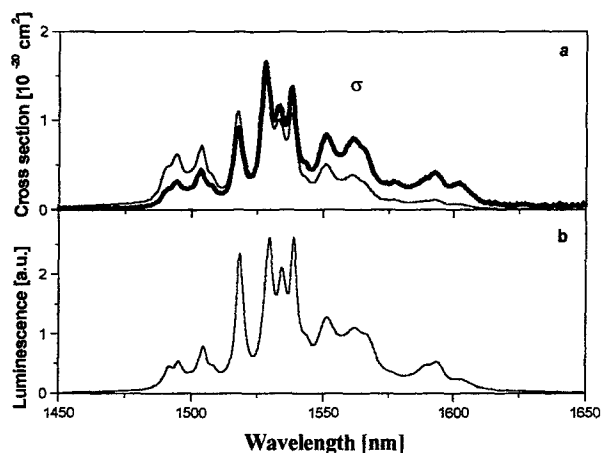


Fig. 5 a) absorption cross section (solid line) and calculated spectra and emission cross section (bold line) b) luminescence spectra recorded for  $^4I_{13/2} - ^4I_{15/2}$  under excitation by Ti:sapphire laser emitting at 970 nm. All spectra for  $\sigma$  polarisation

cross section  $\sigma_{em}(\lambda)$  for  $\pi$  and  $\sigma$  polarisation is indicated by bold lines in Fig. 4a and Fig. 5a, respectively. Corresponding  $\sigma_a(\lambda)$  spectra are also given by solid lines in those figures. The luminescence spectra for  $\pi$  and  $\sigma$  polarisation recorded under excitation by Ti:sapphire laser emitting at 970 nm are presented in Fig. 4b and Fig. 5b. It can be seen that spectra derived by reciprocity method are in a good agreement with luminescence spectra recorded for both  $\pi$  and  $\sigma$  polarisation. From the estimated  $\sigma_a(\lambda)$  and  $\sigma_{em}(\lambda)$  the gain coefficient  $G(\lambda)$  was calculated using formula<sup>10</sup>:

$$G(\lambda) = N[P\sigma_{em}(\lambda) - (1 - P)\sigma_a(\lambda)] \quad (7)$$

where  $N$  is the  $Er^{3+}$  concentration,  $P$  is a population inversion parameter defined as a density of ions in upper state divided by  $N$ . Results of calculation for several reasonable values of  $P$  are shown in Fig. 6. The presented results are consistent with that presented by F.S. Ermeneux at al.<sup>1</sup> and suggest the possible application of Er:YVO<sub>4</sub> as a laser material operating near 1.6  $\mu m$ .

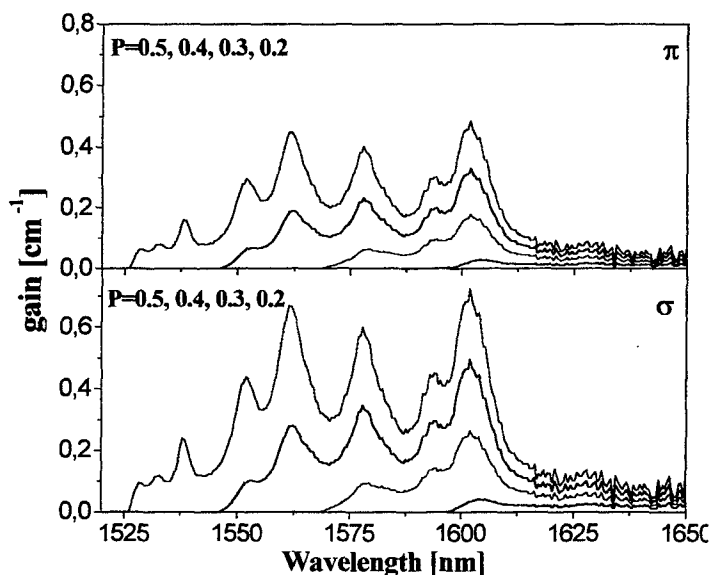


Fig. 6 Gain coefficient calculated for several reasonable values of  $P$  for  $^4I_{13/2} - ^4I_{15/2}$  transition  $Er^{3+}$  in YVO<sub>4</sub>

#### 4. CONCLUSION

The theoretical approach basis on multiphonon relaxation model cannot predict the experimental temperature dependence of lifetime for the  $^4S_{3/2}$  level. The participation of the ESA process from  $^4I_{13/2}$  in upconverted green phenomenon under excitation at 970 nm is appreciable. The emission cross section spectra derived by reciprocity method are consistent with recorded luminescence spectra of  $^4I_{13/2} - ^4I_{15/2}$  transition for both  $\pi$  and  $\sigma$  polarisation. The positive gain coefficient for  $^4I_{13/2} - ^4I_{15/2}$  transition suggest the possible application of Er:YVO<sub>4</sub> as a laser material operating near 1.6  $\mu m$ .

#### ACKNOWLEDGMENTS

This work is supported by The Polish Committee for Scientific Research under grant No. 8T 11B 021 17

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